Insulator – Insulator Contact Charging and its Relationship to Atmospheric Pressure

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Abstract— **Metal-metal and metal-insulator contact charging are well known phenomena with good theoretical understanding. However, insulator-insulator charging is not as well understood. Surface ion exchange is suspected of being the mechanism of insulator-insulator triboelectric charging. Experiments have shown that the amount of charge exchange is highly dependent on the atmospheric pressure of the gas. We present a two-phase model based on an ideal gas of singly-charged ions in equilibrium with a submonolayer adsorbed film.**

I. INTRODUCTION

In spite of its great importance in industrial processes, insulator-insulator charging is the least understood triboelectric phenomenon [1]. Insulator–insulator charging, however, is of great concern for spacecraft in deep space or on planetary surfaces [2]. Since insulators do not have mobile electrons in conduction bands, attempts have been made [3][4] to explain or study the insu-

lator-insulator charge exchange mechanism using methods other than electron exchange. In our paper, we present a model of the electrostatic charging of materials where we model the electric double layer as a submonolayer adsorbed film of ions in equilibrium with a vapor of singly-charged particles.

II. BACKGROUND

Charging by metal to metal contact is readily understood as an exchange of electrons due to the difference in the metal work functions. Electrons in a metal of higher energy levels can lower their energy by moving to a metal with lower energy levels. Charge Q is given by $Q = VC$, where V is the potential and C is the geometry-dependent capacitance of the system. For metal - metal charging, the above equation can be rewritten as

$$Q = \frac{(\phi_A - \phi_B)}{q_e} C \qquad (1)$$

where $\phi_A - \phi_B$ is the difference in the work functions of metals A and B, and q_e is the electron charge (1.602×10^{-19} Coulombs).

Metal-insulator contact charging was found to be linearly proportional (with some exceptions) to the metal work function when tested with polymers [5][1]. This allowed an effective work function to be assigned to the polymers. Electron transfer is theorized to be between the metals' Fermi level and localized energy levels in the band gap of the insulator [6][1]. These localized energy levels in the insulator can be formed by impurities in the insulator, surface states, and defects in the crystal structure. The transferred charge equation would be the same as equation (1) above except that one of the metal work functions would be replaced by the effective work function of the polymer [7]. Using these insulator work functions, Davies [8] developed a triboelectric series to explain the sign and magnitude of charge expected between insulator-insulator contacts. Davies provided experimental verification of this and additional data was provided by Strella (unpublished data referenced in [9]) that in general agree with Davies' values.

There are however, problems with the electron-transfer view for metal-insulator charging. Electrons in insulators do not have single energy levels as they do in conductive metals. The energy of an electron in an insulator is a function of its physical position, surface impurities, and the materials' chemical and atomic structure. Thus, the work function for an insulator can only be determined by experiment [5]. Other works show that there is not a linear relationship between surface charge and the metal work function unless there are multiple contacts with elastic deformation, resulting in a change in the area of contact [10][11]. However, the common practice is to use the effective poly-

mer work function for insulators to determine the charge exchange after insulator-insulator contact.

A possible mechanism for contact charging is ion exchange. Surface impurities, which can be mostly ionic in nature, will also play a role in the charging of insulators. Ion transfer in metal-insulator charging has been advocated by several researchers [12][13][14] to account for charge exchange. Ions can exist on the surface of a insulator either in weak bonds due to intermolecular forces while residing in vibrational energy states [1] or as solvated ions in a thin surface water layer [15].

Many materials are hydrophilic and have thin layers of water molecules on their surfaces. The thickness of this water layer varies from several hundred angstroms (Å) for materials in very humid environments at atmospheric pressure to about ten Å for materials in high vacuum chambers [1]. This solid/aqueous interface can be treated as an electrical double layer with solvated ions in the water that are chemically adsorbed on surfaces. These ions can include Na^+, Cl^-, OH^-, etc. The net charge on the surface of the solid material would be balanced by an opposite charge of ions in the water layer at the solid/aqueous interface, hence the name electrical double layer [15].

The contact between two surfaces is mostly between the surface double layers unless large contact force and/or rubbing are used. If the two electric double layers are at different potentials, then a rearrangement of the distribution of the solvated ions can take place giving each surface a net (and opposite) charge after separation. This electrolytic view of triboelectrification was favored by Freundlich [16].

III. EXPERIMENTAL DATA ON PRESSURE DEPENDENCE OF CONTACT CHARGING

Experiments have been performed by Matsuyama and Yamamoto [17] where they measured the charges generated on a metal plate by impact with a polymeric particle. They found that the charges developed on the particle were limited by the Paschen limit.

The Paschen Discharge Limit or Paschen's Law was derived to explain the maximum electrical field sustainable in a gas between two metal electrodes [18]. The critical discharge potential is a function of several factors such as the gas species, gas pressure, humidity, electrode metal, and electrode separation [19]. A Paschen curve is typically graphed as discharge or sparking potential voltage versus the product of gas pressure and electrode separation. The discharge voltage decreases with pressure to a minimum value because, as pressure decreases, the mean free path between collisions increases, allowing

for a greater charged particle kinetic energy to develop. The Paschen curve then increases from the minimum due to a lack of mediating gas atoms to be ionized. The Paschen curve represents the maximum strength of an electric field allowed in a gas at the particular set of factors mentioned above. Stronger fields will result in either corona discharge to the air or sparking discharge between the electrodes.

In Matsuyama's experiments [17], charged polymer particles bombard a metal plate and the net charge is measured with a Faraday cup. After striking the metal plate, the particle acquires enough charge to exceed Paschen's curve upon separation and thus is forced to lose some charge to gaseous discharge. The remaining charge on the particle is below the Paschen limit but still higher than the initial charge. Figure 1 shows the particle potential as a function of the distance from the plate.
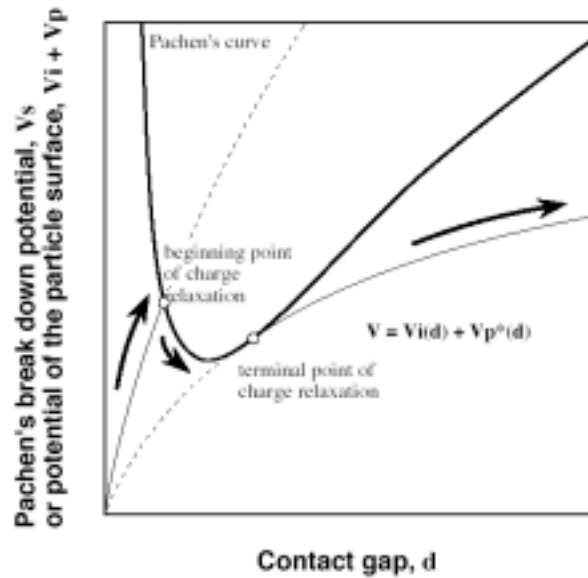

Fig. 1. Particle potential as a function of the distance from the plate [17].

This pressure dependent charging scheme has guided experiments performed in our laboratory to show the pressure-dependence on triboelectric contact charging [20]. Seven polymer insulators that span the triboelectric series were mounted on a wheel inside a bell jar vacuum chamber. These polymers were brought into rubbing contact with wool and Teflon targets respectively. Electric field data was measured by a JCI 140 CF Electrometer at four pressures for each target material. This data is given in Figure 2. As can be seen, the amount of charging decreases with decreasing pressure. Therefore, pressure

may play a vital role in determining the residual charge remaining on the surface. For comparison, the Paschen Limit for Aluminum electrodes in air was plotted in terms of surface charge on Figure 2.
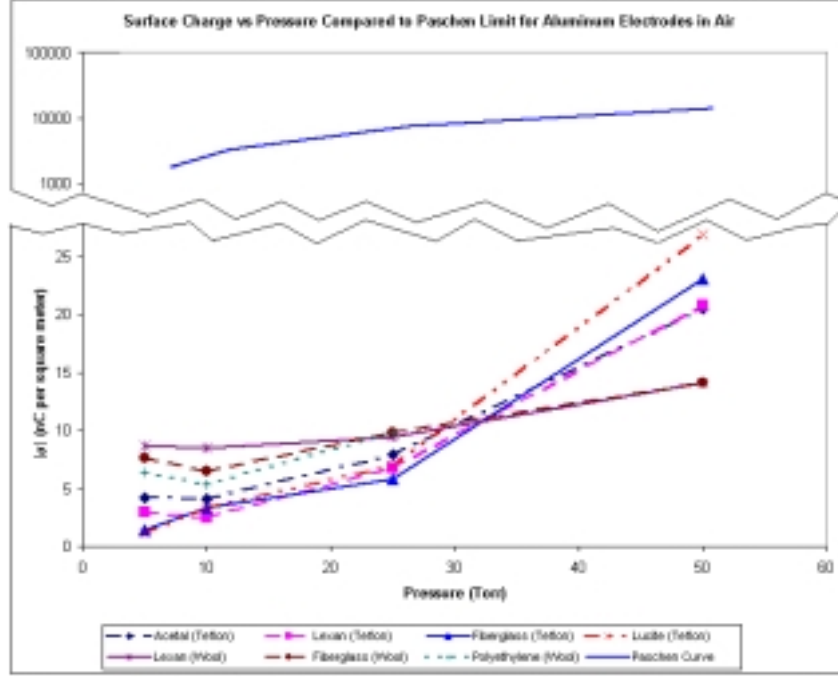

Fig. 2. Polymers rubbed with Teflon and wool showing surface charge dependence on pressure and compared to the Paschen Limit for Aluminum electrodes in air [18].

IV. TWO-PHASE EQUILIBRIUM MODEL

Since atmospheric pressure and moisture layers play a major role in surface charging, we present a preliminary model in which the surface of the insulator is in equilibrium with its external environment. Equilibrium is used because charge transfer occurs rapidly. The surface is modeled as having localized states with a certain adsorption energy, $-\xi_0$, for the surface particles. The particles are considered to be a vapor of non-interacting ions of single polarity in equilibrium with an adsorbed submonolayer on the surface. The chemical potential of the vapor is determined using the Grand Canonical ensemble and then equated to the chemical potential of the submonolayer to determine vapor pressure. By assigning a charge (assuming single ionization) to the vapor particles, the surface charge resulting from the adsorbed monolayer can be calculated as a function of pressure.

Assuming that there are N total sites on the surface that can be occupied by ions and that n of these sites are occupied, an equation for the chemical potential can be derived using Fermi-Dirac statistics

$$\frac{n}{N} = \frac{1}{e^{(\xi_0 - \mu_S)/k_B T} + 1} \tag{2}$$

where ξ_0 is the adsorption energy of the ion, μ_s, is the chemical potential of the adsorbed film, k_B is Boltzmann's constant, and T is the temperature. First, we solve for the chemical potential of the adsorbed gas, μ_s, using equation (2):

$$\mu_s = -k_B T \ln\left(\frac{N}{n} - 1\right) - \xi_0 \tag{3}$$

Next, the gas phase chemical potential, μ_g, can be calculated using the partition function. The partition function for one particle is given by

$$z = \frac{1}{h^3} \int\limits_V \int\limits_{-\infty}^{\infty} e^{-H/k_B T} dp^3 dx^3 \tag{4}$$

where H is the kinetic Hamiltonian for the gas particle, $P^2/2m$ and h is Planck's constant (6.63×10^{-34} J · s). Integrating over volume and momentum gives

$$z = \frac{V}{h^3} \left(2\pi m k_B T\right)^{3/2} \tag{5}$$

By using the series expression for e^x, the grand partition function can now be written as

$$Z_G = \sum_n \frac{1}{n!} z^n e^{n\mu_g/k_B T} = \exp\left(z e^{\mu_g/k_B T}\right) \tag{6}$$

The Helmholtz free energy is given by [21]

$$F = -k_B T \ln(Z_G) = -k_B T \frac{V}{h^3} \left(2\pi m k_B T\right)^{3/2} e^{\mu_g/k_B T}. \tag{7}$$

Pressure is given by [21]

$$P = -\left(\frac{\partial F}{\partial V}\right)_{\mu,T} = k_B T \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2} e^{\mu_g/k_B T} \tag{8}$$

Finally, the chemical potential of the gas is

$$\mu_g = k_B T \ln\left[P\left(\frac{1}{k_B T}\right)^{5/2} \left(\frac{2\pi\hbar^2}{m}\right)^{3/2} \right]. \qquad (9)$$

Setting $\mu_s = \mu_g$, (equations (3) and (9)), and solving for the vapor pressure, $P = P_V$, gives

$$P_V = (k_B T)^{5/2} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \left(\frac{1}{\frac{N}{n}-1}\right) e^{-\xi_0/k_B T}. \qquad (10)$$

The total charge on the surface is just the number of surface sites occupied by ions or n. Solving the above equation for n gives.

$$n = \frac{NP_V}{(k_B T)^{5/2} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{-\xi_0/k_B T} + P_V}. \qquad (11)$$

Another expression for n can be developed from Gauss' Law for the total enclosed charge, Q, on a surface

$$Q = \varepsilon_0 E A \qquad (12)$$

where E is the electric field, A is the surface area, and ε_0 is the electrical permittivity of free space. Q can be written as the number of surface ions (assuming single ionization) times the electronic charge, which gives us

$$n q_e = \varepsilon_0 E A \qquad (13)$$

$$n = \frac{\varepsilon_0 E A}{q_e} = \frac{\sigma A}{q_e} \qquad (14)$$

Setting equations (11) and (14) equal gives the following relationship for the surface charge on the film of adsorbed particles in terms of vapor pressure, temperature, adsorption energy, and ion mass:

$$\sigma = \frac{q_e N}{A} \frac{P_V}{(k_B T)^{5/2} \left(\dfrac{m}{2\pi \hbar^2}\right)^{3/2} e^{-\xi_0/k_B T} + P_V} \tag{15}$$

V.   RESULTS

In order to compare the importance of atmospheric pressure on insulator charging using our model (15), experiments were performed using the Mars Environmental Compatibility Assessment (MECA) electrometer developed by KSC and the Jet Propulsion Laboratory [2]. The MECA electrometer contains five polymers backed with electrodes to measure charge exchange between insulator–insulator contact. In a series of experiments, the MECA electrometer was charged up triboelectrically using wool in a vacuum chamber and then the pressure was lowered. The polymers on the electrometer discharged in a stair step fashion indicating that patches of charge left the surface. An example of this data is shown in Figure 3.
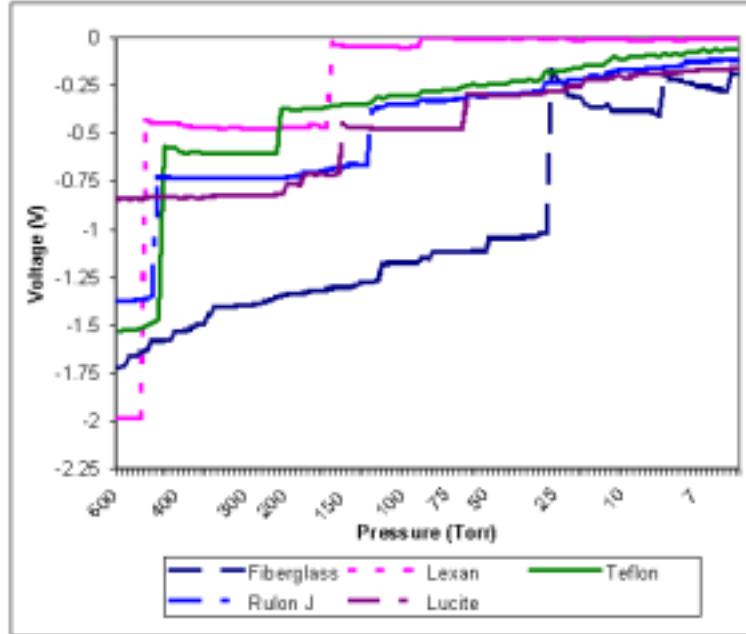

Fig. 3. Experimental Data Showing Step-Like Charge Decay of the MECA Electrometer with Decreasing Pressure.

The data points of the highest corners of the stair steps from Figure 3 for each polymer are graphed versus pressure in Figure 4, showing the relationship between maximum surface charge and pressure.
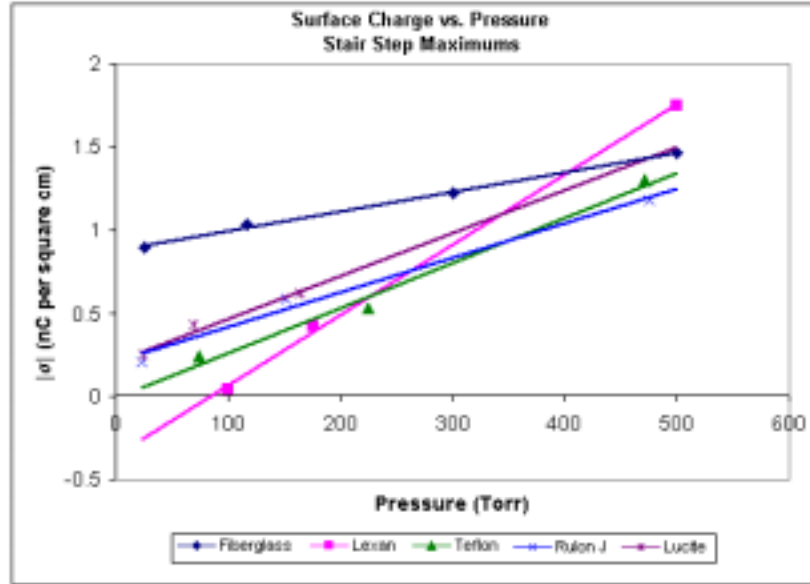

Fig. 4. Maximum surface charge data from stair step curves showing nature of discharge with decreasing pressure.

The curve fits to the experimental data in Figure 4 are from our expression, equation (15). The fitting parameters used in equation (15) (shown in Table 1) provide values for the adsorption energies and number of occupiable charge sites per unit area at room temperature (300 K). Thus it may be possible to determine the amount of charge deposited on insulators after insulator-insulator contact, if these two parameters are known. The atomic species chosen was the Sodium ion (Na^+, $m = 3.82 \times 10^{-26}$ kg) because NaCl is one of the most easily (and common) solvated ionic compounds. It is interesting to note that Teflon and Rulon J, which are variants of the same polymer, have similar adsorption energies.

TABLE 1: FITTING PARAMETERS FOR EQ. (15) COMPARED TO
REPORTED VALUES OF ($\phi_A - \phi_B$)

Material	Adsorp. Energy, ξ_0 (eV)	$q_e N/A$ (C/m^2)	Davies [22] ($\phi_A - \phi_B$) (eV)	Akande & Adedoyin [23] ($\phi_A - \phi_B$) (eV)
Fiberglass	-0.312	3000		
Lexan	-0.33	10,586.7	-0.34	
Teflon (PTFE)	-0.321	4,818.69	-0.34	
Rulon J	-0.321	3,697.77		
Lucite (PMMA)	-0.327	3,656.91		-1.40
PVC			0.25	
Polyimide			-0.24	
PET			-0.35	
Polystyrene			-0.38	-0.23
Nylon 66			-0.52	

Table 1 shows the adsorption energies and *qeN/A* using the MECA as well as measured values of ϕ from Davies [22] and Akande *et al.*, [23], for several polymers using Gold ($\phi = 4.6$ eV) as the reference metal. *As* one can see from table 1, the values of ξ_0 correspond to the difference of the work functions, ($\phi_A - \phi_B$), measured for metal-insulator contact. Conventionally, insulators are assigned "effective work functions" based on their charging properties against metals of known work function. Therefore it is believed that charging of two insulators could be determined by comparing their effective work functions. However, Davies [22] has shown that the work function for several polymers is very similar. Polymers with nearly identical work functions may acquire very different contact charges. This cannot be explained using the electron transfer

model. In fact, Schein [24] has stated that if the mechanism is the same for metal-insulator contact as it is for insulator-insulator contact, then electrons cannot be transferred since insulators do not contain mobile electrons.

Thus we present an alternative method for determining the amount of charge transferred between insulators. Here the mechanism is that of ion transfer as opposed to electron transfer. Experiments indicate that surface properties, such as hydrophobicity, play a key role. Our model focuses on identifying the source and meaning of the adsorption energies for insulators. We interpret the work function of the polymer to be the adsorption energy of ions bound to the surface. Determination of insulator work functions by contact with a metal is equivalent to our determination of the adsorption energy. Thus, charging an insulator and removing the vapor pressure provides an alternative method for determining ($\phi_A - \phi_B$), the difference of work functions. We believe that this interpretation provides a clearer picture of the phenomenon.

The differential charging of these polymers may be due (in part) to the difference in available surface states developed by the curve fit in Table 1. Having more or less sites available for a certain ionic species can lead to differential charging of the surfaces if that species is present.

VI. FUTURE WORK

Future work must interpret the surface adsorption energy range and the number of surface sites per unit area. The vapor will be modeled as a gas of positive and negative particles. In air, there are, on average, 5.0×10^8 ions per cubic meter [25]. These ions will occupy some of the N sites on a surface and form an electric field which will attract or repel other ions.

More triboelectric testing will be performed with charge measured as a function of pressure as in figure 3. The number of materials will be increased to give a more comprehensive data set.

The Paschen discharge curve for polymers may be different than for metallic surfaces. For metal electrodes, electrons are ejected from the cathode when positive ions impact with kinetic energy equal to at least twice the work function [26] and contribute to the breakdown cascade [27]. Polymers do not have conduction band electrons to be ejected unless the polymer is heated to the point of ionization. A Paschen discharge experiment is being developed at the Kennedy Space Center (KSC) to measure the discharge voltage of thin polymer sheets placed between metal electrodes at various gas pressures.

Other planned experiments will expose polymeric materials to electrolytic fluids such as salt (NaCl) water and also deionized water to determine the effect

of varying the surface ionic content on contact charging. Also, the effects of temperature will be examined in these experiments.

VII. CONCLUSION

Insulator-insulator contact charging is the least understood triboelectric phenomenon. We have described some of the current theories on insulator-insulator contact charging and have put forward a two-phase equilibrium model for surface charge. The model is in general agreement with models of metal-insulator contact charging. However, the mechanism is that of ions as opposed to electrons. More experimentation is planned to expand the data set currently available.

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